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(54) Process for preparing functionalized perfluoropolyoxyalkylenes.

(57) A process for preparing functionalized perfluoropolyoxyalkylenes, wherein the corresponding perfluoropolyoxyalkylenes containing peroxy bonds in the chain are reacted with a primary or a secondary alcohol, or mixtures of these alcohols, in the presence of a catalyst selected from iodine, hydriodic acid or alkaline metal iodides.
The process leads to the obtainment of perfluoropolyoxyalkylenes having a high functionalization degree, which can be easily purified by removing the excess of alcohol through distillation.

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The present invention relates to a process for preparing functionalized perfluoropolyoxyalkylenes via reduction of perfluoropolyoxyalkylenes containing peroxy bonds in the chain.

High molecular weight perfluoropolyoxyalkylenes having peroxy bonds -O-O- along the chain are products well known in the art. Said products can be converted, through reduction of the peroxy bonds, into controlled molecular weight perfluoropolyoxyalkylene compounds having end groups functionalized with carboxylic groups and/or ketonic groups, or functional groups derived therefrom, such as acyl halides, esters, amides, nitriles, carboxylated groups, hemiketals, etc.

Functionalized perfluoropolyoxyalkylenes are described, for example, in U.S. patents Nos. 4,085,137; 4,721,795 and 4,757,145. They are used in several fields either as such (for example as lubricants or as protective agents for lapideous materials or for metals), or as starting compounds for the synthesis of other fluorinated products, and in particular of condensation polymers, endowed with unusual chemico-physical characteristics, such as thermal stability, chemical inertia, high flexibility even at very low temperatures, etc.

In view of such utilizations it is of substantial importance to provide a process for the reduction of the peroxide bridges, which can be easily practised on an industrial scale and which leads to the obtainment of products having the highest possible purity degree as well as a high functionalization degree.

U.S. patent No. 3,847,978 describes a broad class of products which can act as reducing agents for the peroxide bridges, among which: molecular hydrogen, nascent hydrogen; primary or secondary alcohols, either alone or in the presence of aluminium alcoholates; metal hydrides or complexes thereof; sulphur dioxide; sulphydric acid or sulphides; metals, such as iron or tin, in the presence of a strong acid; hydriodic acid, and still other products.

In the industrial practice, all these reducing agents permit to obtain satisfactory results, both due to the too low reaction rate and due to the formation of by-products, which reduce the purity degree and the functionalized product yields.

One of the utilized processes comprises the use of SO_2 as a reducing agent, in the presence of catalytic amounts of I_2 or HI. Such process, although it provides perfluoropolyoxyalkylenes endowed with a high functionalization degree, gives rise to SO_3, a chemically aggressive substance, which must be removed from the final product by means of repeated washings, what lowers the final yield and rises problems connected with the disposal of the wastes. Analogous problems related to the purification of the final product are encountered if HI is used as a reducing agent, because that leads to the formation of I_2, which too can be removed only by means of repeated washings.

A further disadvantage of the above-mentioned processes derives from the use of chlorofluorocarbons, for example CFC 113 (CCl_2F-$CClF_2$), as a reaction medium, what involves environmental problems, particularly as regards the ozone layer of the atmoshpere.

As already mentioned, U.S. patent No. 3,847,978 suggests to use, as reducing agents, primary or secondary alcohols, such as methanol, ethanol, isopropanol. Apart from the fact that with the alcohols suggested by the above-said patent the reaction rate is very low (for example, if methanol is used, the reaction is completed only after 30 hours at reflux), the reaction with alcohols gives rise to high amounts of hydrogenated end groups of the type -CF_2H, with consequent lowering of the functionalization degree of the final products and loss of a carbon atom.

It has now surprisingly been found that the reaction for reducing perfluoropolyoxyalkylene containing peroxy bonds in the chain can be advantageously conducted with primary or secondary alcohols, in the presence of a catalyst selected from iodine, hydriodic acid or alkaline metal iodides, with formation of high-functionalization-degree perfluoropolyoxyalkylenes, which can be easily purified by removing the alcohol in excess through distillation.

Thus, it is an object of the present invention to provide a process for preparing functionalized perfluoropolyoxyalkylenes, which comprises reacting the corresponding perfluoropolyoxyalkylenes containing peroxy bonds in the chain with a primary or secondary alcohol R-OH, or mixtures of these alcohols, in the presence of a catalyst selected from iodine, hydriodic acid or iodides of alkaline metals.

The peroxy perfluoropolyoxyalkylenes utilized as starting products are preparable in accordance with what is described, for example, in GB patents Nos. 1,226,566 and 1,104,482 and correspond to the general formula:

$$A\text{-}O\text{-}(C_3F_6O)_m\text{-}(C_2F_4O)_n\text{-}(CFXO)_p\text{-}(O)_q\text{-}B \qquad (I)$$

where:

A and B, like or different from each other, are end groups selected from: -COF, -CF_2-COF, -$CF(CF_3)$-COF, -CF_2-CO-CF_3, -CF_2CF_2-COF, -CF_3, -C_2F_5, -C_3F_7, -CF_2Cl, -C_2F_4Cl, -C_3F_6Cl;

X is selected from: -F, -CF_3;

m, n, p are integers, like or different fron one another, ranging from 0 to 100, provided that $m + n > 0$;

q ranges from 1 to 90, provided that $(m + n + p) > q$;

the various repeating units $-C_3F_6O-$, $-C_2F_4O$, $-CFXO-$ and -O-being statistically distributed along the chain.

In particular, depending on the type of monomers which are present in the chain, the variables m, n, p and q can assume the following values:

(1) when n = O:
-X = -F; $-CF_3$; m/p > 3; (m+p)/q = 2-100;
(2) when m = O:
-X = -F; n/p = 0.02 - 50; (n+p)/q = 2-1,000;
(3) when m, n, p are other than zero:
m/p = 0.02 - 50; m/(n+p) = 0.02-50; (m+n+p)/q = 2-1,000.

The perfluoropolyoxyalkylene containing peroxide bridges can be utilized as such if the peroxide oxygen content is already at the desired values as a function of the molecular weight of the functionalized perfluoropolyoxyalkylene compound to be obtained. If the precursor has a peroxide oxygen content which exceeds the one desired, it can be reduced by subjecting the product to a thermal or photochemical treatment according to what is described for example, in U.S. patent No. 4,668,357 or in patent application EP 340,739.

As reducing agents it is possible to utilize all the primary or secondary alcohols R-OH, in which R is a straight or branched alkyl or cycloalkyl radical having 1 to 12 carbon atoms. Among them, there are utilizable, for example: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol, 2-hexanol, cyclohexanol, 1-dodecanol, 2-dodecanol, etc., or mixtures thereof. The alcohol is used in such amounts that the molar ratio between alcohol and peroxide oxygen (q) generally ranges from 4 to 200, preferably from 10 to 150.

In a preferred embodiment there are used, as reducing agents, the primary alcohols having 4 to 6 carbon atoms or the secondary cycloalkyl alcohols having 5 to 8 carbon atoms. The use of such alcohols permits to sensibly increase the reaction rate so as to obtain a complete conversion in 3-5 hours at the reflux temperature of the alcohol. Particularly preferred are 1-butanol and cyclohexanol.

The reaction is conducted in the presence of catalytic amounts of iodine, hydriodic acid or alkaline metal iodides. By "catalytic amounts" are generally meant such catalyst amounts wherefore the ratio between moles of iodine I and moles of peroxide oxygen (q) ranges from 0.01 to 0.5, preferably from 0.01 to 0.35. Examples of alkaline metal iodides utilizable as catalysts are potassium iodide and sodium iodide.

It is to be noted that the catalyst has not the function of increasing the total reduction reaction rate, but of directing the reaction towards the obtainment of functionalized end groups, fully avoiding the formation of hydrogenated end groups $-CF_2H$. In this way it is possible to completely convert the starting peroxide product into a mixture of perfluoropolyoxyalkylenes functionalized at the ends with ester groups:

$-CF_2COOR$,

$$-\underset{\displaystyle CF_3}{\underset{|}{C}}F-COOR,$$

or ketonic groups:

$-CF_2-CO-CF_3$.

Such end groups can be easily converted, through well known reactions of the art (see for example U.S. patent No. 3,810,874), into other reactive functions, such as carboxylic, acylic, amidic, nitrilic, carboxylated, hemiketalic, alcoholic groups, etc.

The process of the present invention is advantageously conducted by using the alcohol itself as a reaction medium: in this way it is possible to avoid using other solvents, such as the chlorofluorocarbons, with considerable advantages as regards both the simplicity and profitability of the process and possible problems connected with the environmental pollution. However, that does not exclude the possibility of practising the process using, as a reaction medium, other solvents, such as carboxylic acids, perfluoropolyethereal alcohols, perfluoropolyethereal esters, etc. The reaction is generally conducted at the reaction medium reflux temperature, so that it is depending on the type of the utilized alcohol and/or solvent; generally, the reaction temperature ranges from 50° to 150°C, while the pressure is generally in the range of from 1 to 10 atm.

At the end of the reaction, the final product can be easily isolated and purified through distillation, preferably at reduced pressure, of the unreacted alcohol.

The following examples are given to better illustrate the present invention, but they are not to be construed as limitative of the scope thereof.

EXAMPLE 1

260 g of 1-butanol, 1 g of iodine and 200 g of a peroxy perfluoropolyoxyalkylene corresponding to general formula (I), wherein m = 0, -X = -F, (n+p)/q = 13.06 and n/p = 1.14, having an average molecular weight equal to 82,000, were charged, at room temperature, into a 1 l reactor. Through ^{19}F NMR analysis, the following composi-

tion for end groups A and B was determined: -COF (28%), $-CF_2COF$ (17%), $-CF_3$ (32%), $-CF_2Cl$ (12%), $-C_2F_4Cl$ (11%).

The reaction mixture was subjected to stirring and was heated to reflux temperature in a thermostatic bath over the course of 5 hours. On conclusion of the reaction, the alcohol in excess was removed by distillation up to 100 °C at a reduced pressure of 10^{-2} millibars. There were obtained 199.7 g (yield 99.8%) of perfluoropolyoxyalkylene product, which, on ^{19}F NMR analysis, resulted to be free from peroxy groups and exhibited an average molecular weight equal to 1,260 and a n/p ratio equal to 1.05. The end groups had the following distribution: $-CF_2COO(CH_2)_3CH_3$ - (98.5%), $-CF_3$ (0.9%), $-CF_2Cl$ (0.3%), $-C_2F_4Cl$ (0.3%). $-CF_2H$ end groups were absent.

EXAMPLE 2 (comparative)

200 g of the peroxy perfluoropolyoxyalkylene of example 1 and 260 g of 1-butanol were charged into a 1 liter reactor at room temperature.

The reaction mixture was stirred and heated to reflux temperature in a thermostatic bath during 5 hours. At the end of the reaction, the alcohol in excess was removed by distillation at reduced pressure. There were obtained 193 g of product (yield: 96.5%), which, on ^{19}F NMR analysis, resulted to be free from peroxy groups and exhibited an average molecular weight equal to 1,200 and a n/p ratio equal to 1.04. The end groups were distributed as follows:
$-CF_2COO(CH_2)_3CH_3$ (72.4%), $-CF_2H$ (26.3%), $-CF_3$ (0.8%), $-CF_2Cl$ (0.3%), $-C_2F_4Cl$ (0.2%).

EXAMPLE 3

200 g of the peroxy perfluoropolyoxyalkylene utilized in example 1, 260 g of 2-butanol and 1 g of I_2 were charged into a 1 liter reactor. The mixture was stirred and heated for 15 hours to reflux temperature in a thermostatic bath. At the end of the reaction, the unreacted alcohol was removed by distillation at reduced pressure. Obtained were 197.5 g (yield: 98.7%) of perfluoropolyoxyalkylene product, which, on ^{19}F NMR analysis, resulted to be a 2-butanol diester, free from peroxy bridges and from $-CF_2H$ end groups.
The average molecular weight was equal to 1,230.

EXAMPLE 4

Following the same procedure of example 3, there were reacted 20 g of the peroxy perfluoropolyoxyalkylene utilized in example 1, 65 g of 1-dodecanol and 0.1 g of I_2. By heating under stirring in a thermostatic bath at 130 °C for 10 hours, 84.3 g of product were obtained. After removal, under vacuum, of the unreacted alcohol, 19,8 g (yield = 99%) of perfluoropolyoxyalkylene product were obtained, which, subjected to ^{19}F NMR analysis, resulted to be a 1-dodecanol diester, free from peroxy bridges and from $-CF_2H$ end groups.
The average molecular weight was equal to 1,350.

EXAMPLE 5

200 g of the peroxy perfluoropolyoxyalkylene utilized in example 1, 350 g of cyclohexanol and 1 g of I_2 were charged into a 1 liter reactor. The mixture was stirred and it was heated for 3 hours at a temperature of 120 °C in a thermostatic bath. On conclusion of the reaction, the unreacted alcohol was removed by distillation at reduced pressure. There were obtained 199.5 g (yield: 99.7%) of perfluoropolyoxyalkylene product which, on ^{19}F NMR analysis, resulted to be a cyclohexanol diester free from peroxide bridges and of $-CF_2H$ ends groups. The average molecular weight was equal to 1,230.

EXAMPLE 6

260 g of 1-butanol, 1 g of iodine and 200 g of a perfluoropolyoxyalkylene corresponding to general formula (I), where n = O, (m + p)/q = 49.3 and m/p = 23.3, having an average molecular weight equal to 565, were introduced into a 1 liter reactor. By means of ^{19}F NMR analysis, the following composition for end groups A and B was determined:
-COF (9.5%), $-CF_2COF$ (45%), $-CF_3$ (3.5%), $-C_3F_6Cl$ (42%).

The reaction mixture was subjected to stirring and heated to reflux temperature in a thermostatic bath for 5 hours. At the end of the reaction, after removal of the alcohol in excess by distillation at reduced pressure, there were obtained 197.9 g (yield = 98.9%) of perfluoropolyoxyalkylene product, which, on ^{19}F NMR analysis, resulted to be free from peroxy groups and exhibited an average molecular weight equal to 535 and a m/p ratio = 23. The end groups had the following distribution: $-CF_2COO(CH_2)_3CH_3$ (51.5%), $-CF(CF_3)COO(CH_2)_3CH_3$ (2.5%), $-CF_2COCF_3$ (3%), $-CF_3$ (3.3%), $-C_3F_6Cl$ (39.7%). $-CF_2H$ end groups were absent.

EXAMPLE 7

260 g of 1-butanol, 1 g of iodine and 200 g of a perfluoropolyoxyalkylene corresponding to general formula (I), where m, n, p are other than zero, (m + n + p)/q = 13.0, n/p = 4.8, m/(n + p) = 1.03, and having an average molecular weight equal to 2,950, were charged into a 1 liter reactor at room

temperature. Through ^{19}F NMR analysis, the following composition was determined for end groups A and B: $-COF$ (47%), $-CF_3$ (53%).

The reaction mixture was subjected to stirring and was heated to reflux temperature in a thermostatic bath during 5 hours. At the end of the reaction, after the alcohol in excess had been removed by distillation at reduced pressure, there were obtained 199.3 g (yield = 99.6%) of perfluoropolyoxyalkylene product, which, on ^{19}F NMR analysis, resulted to be free from peroxy groups and exhibited an average molecular weight equal to 1,200 and n/p ratios = 2.8 and m/n+p = 1.5. The end groups had the following composition: $-CF_2COO(CH_2)_3CH_3$ (50%), $-CF(CF_3)COO(CH_2)_3CH_3$ (15%), $-CF_2COCF_3$ (8.5%), $-CF_3$ (26.5%). No end groups $-CF_2H$ were present.

Claims

1. A process for preparing functionalized perfluoropolyoxyalkylenes, which comprises reacting the corresponding perfluoropolyoxyalkylenes containing, in the chain, peroxy bonds with a primary or a secondary alcohol R-OH, or mixtures thereof, where R is a straight or branched alkyl or cycloalkyl radical having 1 to 12 carbon atoms, in the presence of a catalyst selected from iodine, hydriodic acid or alkaline metal iodides.

2. The process of claim 1, wherein the perfluoropolyoxyalkylenes containing peroxy bonds in the chain have the general formula:

$$A\text{-}O\text{-}(C_3F_6O)_m\text{-}(C_2F_40)_n\text{-}(CFXO)_p\text{-}(O)_q\text{-}B \qquad (I)$$

where:
A and B, like or different from each other, are end groups selected from: $-COF$, $-CF_2-COF$, $-CF(CF_3)-COF$, $-CF_2-CO-CF_3$, $-CF_2CF_2-COF$, $-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$;
X is selected from: $-F$, $-CF_3$,
m, n, p are integers, like or different from one another, comprised between 0 and 100, on conditions that $m+n>0$; q is comprised between 1 and 90, on conditions that $(m+n+p)>q$; the various repeating units $-C_3F_6O-$, $-C_2F_4O$, $-CFXO-$ and $-O-$ being statistically distributed along the chain.

3. The process of one of the preceding claims, wherein ROH is a primary alcohol having 4 to 6 carbon atoms, or a secondary cycloalkyl alcohol having 5 to 8 carbon atoms.

4. The process of any of the preceding claims, wherein the molar ratio of alcohol to peroxide oxygen (q) ranges from 4 to 200.

5. The process of claim 4, wherein the molar ratio of alcohol to peroxide oxygen (q) ranges from 10 to 150.

6. The process of any of the preceding claims, wherein the catalyst is utilized in such amounts that the ratio of iodine I moles to peroxide oxygen (q) moles ranges from 0.01 to 0.5.

7. The process of claim 6, wherein the ratio of iodine I moles to peroxide oxygen (q) moles ranges from 0.01 to 0.35.

8. The process of any of the preceding claims, wherein the alcohol is the reaction medium and it is removed by distillation at the end of the reaction.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 10 7615

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 445 738 (AUSIMONT) * page 9, line 29 - line 32; example 11 * ---	1	C07C69/708 C07C67/00 C08G65/32 C08G65/00
D,X	US-A-3 847 978 (D SIANESI ET AL) * column 3 - column 4; claims 24,25; examples 2,19 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C07C C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 September 1994	Heywood, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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